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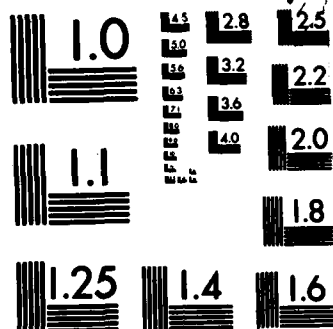   ENGINEERING   P H HOLLOWAY 31 AUG 83 ARO-16492.3-PH
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

In this project, our research has been concentrated on extending the lifetime and applications of electrochromic materials, and upon development of new solid state devices. With respect to lifetime, it is known that this is generally limited by corrosion of WO_3 films in an acid electrolyte. Two mechanisms of corrosion were observed, viz., general dissolution and interfacial delamination. It was found that the dissolution of WO_3 films in acid could be

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20. ABSTRACT CONTINUED

attributed to high concentration of thermodynamically unstable species (WO_2 and W_2O_5) in the as-deposited films. These species were identified by X-ray photoelectron spectroscopy data and are consistent with Rutherford backscattering spectroscopy data which showed an oxygen deficiency (O/W = 2.76). The Pourbaix diagram for tungsten indicated that WO_3 was the thermodynamically stable specie for the present storage condition (pH = 0.5, E = 0.4 V_{SHE}). A corrosion mechanism was proposed consisting of dissolution of WO_2 and W_2O_5 and precipitation of crystalline WO_3 and its hydrates precipitated back onto the original films.

The oxygen content in the WO_3 films was increased by oxygen backfilling during evaporation. Dissolution and interfacial delamination of the oxygen enriched films were reduced to negligible rates due to reduced concentration of WO_2 and W_2O_5. However, the electrochromic properties were degraded by oxygen enrichment. For example, increased resistivity and decreased optical efficiency in the oxygen enriched films resulted in slower coloration speed. The resistivity increase and decreased optical efficiency were explained by postulating an increased density of inactive electron trapping sites. The porosity of the films could be increased by deposition at high background pressure, resulting in increased surface area and absorbed water. The bleaching speeds and self-erasure rates were increased since the rates of removal of protons were increased by the increases in porosity and absorbed water.

In another approach to increase the electrochromic device lifetime, the electrolyte was modified. Devices using a solution of $LiClO_4$ in propylene carbonate exhibited excellent lifetime. Switching speeds were increased by increased porosity, deposition of MgF_2 overlayers, and more conductive indium-tin-oxide layers. In addition, solid state electrochromic devices using a hydrated MgF_2 film were fabricated.

With respect to new applications of electrochromic material, cathochromism of WO_3 films was briefly studied. It was demonstrated that an electron beam can cause local coloration in the material. Parameters such as primary beam energy and current density, electron dose, and film deposition conditions were correlated with optical density and color retention time. It would appear that cathochromism in WO_3 may potentially be useful in pattern generation or information storage.

FINAL REPORT

"Electrically Controlled Coloration

of Materials"

DAAG 29-80-C-0007
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC   27709

Submitted by: Paul H. Holloway
                Department of Materials Science and
                    Engineering
                University of Florida
                Gainesville, FL   32611

Problem Studied

⟶ A select number of solid materials will change color in the visible region of light when an electric field is applied. This phenomenon has been termed electrochromism and it has been the subject of this investigation. ⟵

Summary of Results

In this project, our research has been concentrated on extending the lifetime and applications of electrochromic materials, and upon development of new solid state devices. With respect to lifetime, it is known that this is generally limited by corrosion of WO_3 films in an acid electrolyte. Two mechanisms of corrosion were observed, viz., general dissolution and interfacial delamination. It was found that the dissolution of WO_3 films in acid could be attributed to high concentration of thermodynamically unstable species (WO_2 and W_2O_5) in the as-deposited films. These species were identified by X-ray photoelectron spectroscopy data and are consistent with Rutherford backscattering spectroscopy data which showed an oxygen deficiency ($O/W = 2.76$). The Pourbaix diagram for tungsten indicated that WO_3 was the thermodynamically stable specie for the present storage condition ($pH = 0.5$, $E = 0.4$ V_{SHE}). A corrosion mechanism was proposed consisting of dissolution of WO_2 and W_2O_5 and precipitation of crystalline WO_3 and its hydrates. Interfacial delamination occurred when WO_3 and its hydrates precipitated back onto the original films.

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With respect to new applications of electrochromic material, cathochromism of WO_3 films was briefly studied. It was demonstrated that an electron beam can cause local coloration in the material. Parameters such as primary beam energy and current density, electron dose , and film deposition conditions were correlated with optical density and color retention time. It would appear that cathochromism in WO_3 may potentially be useful in pattern generation or information storage.

LIST OF PUBLICATIONS

1. S.S. Sun and P.H. Holloway, "Modification of Vapor-Deposited WO_3 Electrochromic Films by Oxygen Backfilling," J. Vac. Technol. $\underline{A1}$, 529 (1983).

2. S.S. Sun and P.H. Holloway, "The Effects of Oxygen Stoichiometry Upon the Optical Properties of Vapor-Deposited WO_3 Electrochromic Thin Films," J. Vac. Sci. Technol., to be submitted.

3. S.S. Sun and P.H. Holloway, "Cathodochromism in WO_3 Thin Films," to be submitted.

4. A.R. Haranahalli and P.H. Holloway, "Electrochromism in Neodynium-Doped WO_3," to be submitted.

5. P.H. Holloway and B.J. Molnar, "Electrochromic Response of Tungstates," to be submitted.

6. Sey-Shing Sun, Ph.D. Dissertation, University of Florida, August, 1983.

List of Participating Personnel

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APPENDIX I
"Modification of Vapor-Depositied WO$_3$ Electrochromic
Films by Oxygen Backfilling"

S-S. Sun and P.H. Holloway

J. Vac. Sci. Technol. <u>A1</u>, 529 (1983).

Modification of vapor-deposited WO₃ electrochromic films by oxygen backfilling

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The effects of oxygen backfilling during WO₃ vapor deposition have been studied. Rutherford backscattering and secondary ion mass spectrometry were used to show that the O/W ratio and alkali/W ratio were increased by oxygen backfilling. The durability of the deposited films in H₂SO₄ was shown to be limited by two mechanisms—a general uniform film dissolution and an interfacial attack resulting in delamination. The amount of degradation was reduced as the O/W ratio increased. the electrochromic coloration speed remained unchanged, the bleaching speed and self-erasure rates were faster, and the maximum optical density was lowered for oxygen-enriched films. The mechanisms by which these modifications were achieved are discussed.

PACS numbers: 81.15.Gh, 81.60.Dq, 78.65.Jd

I. INTRODUCTION

Electrochromism, (EC) has been investigated in tungstic oxide thin films for possible application in display devices.[1-3,5] However, there are at least two major problems which prohibit its commercial viability; viz: the slow switching speed and the short device lifetime. The switching has been found to be controlled by oxide film resistivity and oxide/electrolyte interfacial barrier (Helmholtz double layer and Schottky barriers) in coloration.[2,6] Space-charge-limited proton current controls bleaching rates.[2,6] With a thin gold film over tungstic oxide, it is possible to increase the switching speed by at least one order of magnitude.[6] The resulting speed is comparable to that of liquid crystal displays (~50 ms). However, the lifetime of EC devices in aqueous electrolytes is normally short (e.g., ~10⁶ cycles at 0.5 Hz or less than 2 weeks for static storage condition).[2,7]

Two directions have been followed by investigators in trying to improve the lifetime of WO₃ EC devices. the first one involves the use of nonaqueous electrolytes[9,10] (e.g., LiClO₄ in polypropylene carbonate) or solid state electrolytes (e.g., hyrodgen uranyl phosphate).[11,12] Recent reports indicate that studies along this direction have achieved long lifetimes (~10⁷ cycles[5]) and reasonable switching speeds (~300 ms).[5] The second method to improve the device lifetime deals with the modification of the microstructure of WO₃ thin films to improve their stability in acid solutions. As a result, advantage can be taken of the simple fabrication process and fast switching speeds in protonic conducting electrolytes. Arnoldussen has modified evaporated WO₃ thin films with oxygen implantation.[13] This resulted in decreased dissolution rates but the electrochromic response was destroyed. In this paper, a different approach to modifying the film structure will be reported; viz: reactive evaporation of WO₃ in oxygen atmospheres. By such a method, the stability of WO₃ films has been greatly improved without loss of the electrochromic response.

II. EXPERIMENTAL

WO₃ films were prepared by evaporation of 99.9% pure WO₃ powder (Cerac, Inc.) from a resistively heated alumina-

coated tungsten boat. The evaporation system was evacuated to a base pressure of 2×10^{-6} Torr, and WO₃ evaporated either at the residual pressure of 1×10^{-5} Torr, or with partial pressure of oxygen between 5×10^{-5} and 1×10^{-3} Torr. Oxygen partial pressure was controlled by a needle valve. The deposition rate was kept at 10 Å/s. The thickness of the films ranged from 0.2 to 0.4 μm. The substrates were SnO₂-coated glass (NESA from Pittsburgh Plate Glass Company) with a resistance of 100 Ω /□. Some pure graphite planchetes were coated with WO₃ films for Rutherford backscattering spectrometry (Ernest Fullam, Inc.).

Compositional information was obtained from Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS) for measurement of stoichiometry and trace elements, respectively. For RBS, 2 MeV alpha particles with a beam current of 300 nA were used. SIMS was performed in a vacuum system with a residual pressure of 1×10^{-9} Torr. The chamber was backfilled to 1×10^{-5} Torr with argon and 4 keV primary ions at 100 nA were used for analysis. X-ray diffraction patterns from the films were obtained using Philip Electronics Instrument x-ray generator and goniometer. Copper K_α radiation with a nickel filter was used. Topography of the films was determined using a scanning electron microscope (JEOL JSM-35C).

In the corrosion study, the WO₃ films deposited on graphite substrates were immersed in the electrolyte (3.6N H₂SO₄) contained in glass dishes at room temperature. The samples were removed at selected time intervals and examined by RBS. To determine the dissolution rate, the channel number difference between the width of the tungsten RBS peak of a corroded film and an uncorroded film was calculated. The channel number difference was converted into a thickness difference using the calculated stopping power. The dissolution rate was obtained by dividing this thickness difference with time.

The electrochemical properties (switching speed, maximum optical absorption, and open circuit memory) were characterized as reported previously.[6] A potentiostat (Princeton Applied Research Model 173) was used as the power supply. Pt wire and a calomel electrode were used as the
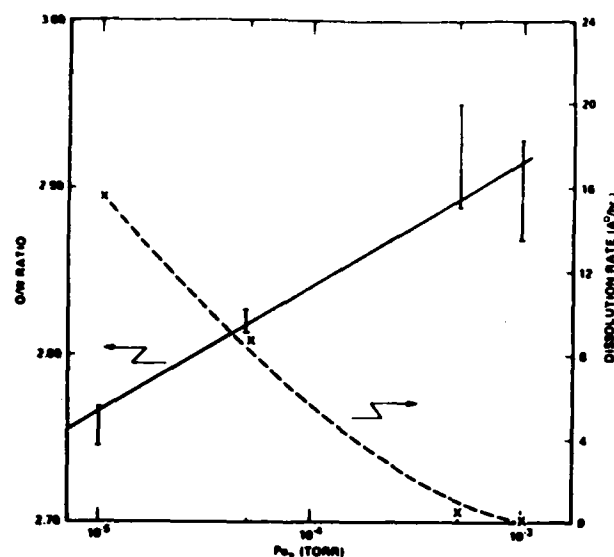
FIG. 1. Oxygen partial pressure vs the oxygen to tungsten atomic ratio or the dissolution rate of WO₃ films in 3.6N H₂SO₄.

TABLE I. Relative signal intensity for Na, K, and H_2O from secondary ion mass spectrometry vs the oxygen partial pressure during deposition of WO_3.

Specie/P_0	1×10^{-5} Torr	5×10^{-5} Torr	5×10^{-4} Torr	1×10^{-3} Torr
Na	1.55	0.89	2.94	3.06
K	0.45	0.81	1.77	1.50
H_2O	0.14	0.03	0.25	0.30

W ratio increased from 2.7 with no oxygen backfilling to 2.9 at $P_{0_2} = 1 \times 10^{-3}$ Torr. SIMS data indicated that the content of water and alkali elements (Na, K) in the films increased with increasing oxygen partial pressure. These samples were examined by AES subsequently and no Na could be detected. Therefore, the alkali concentrations are low, at least below the detection limit ($< 1 \times 10^{19}$ cm^{-3}). As prepared, all films exhibited featureless smooth surfaces under SEM at low magnification (500×). For films prepared at $P_{0_2} = 5 \times 10^{-4}$ Torr, a granular structure was observed at high magnification (3000×). After storage in the electrolyte, WO_3 films began to degrade by two mechanisms—a general uniform dissolution and an interfacial attack resulting in delamination. Figure 1 shows the effect of oxygen backfilling on the dissolution rate based on RBS data for films deposited on graphite planchetes. Films prepared at $P_{0_2} < 5 \times 10^{-4}$ Torr are susceptible to dissolution, while those prepared at $P_{0_2} > 5 \times 10^{-4}$ Torr experienced slower dissolution. Dissolution became negligible at $P_{0_2} = 1 \times 10^{-3}$ Torr. In addition to the general dissolution, interfacial attack was also significant for $P_{0_2} = 5 \times 10^{-5}$ Torr for films on glass
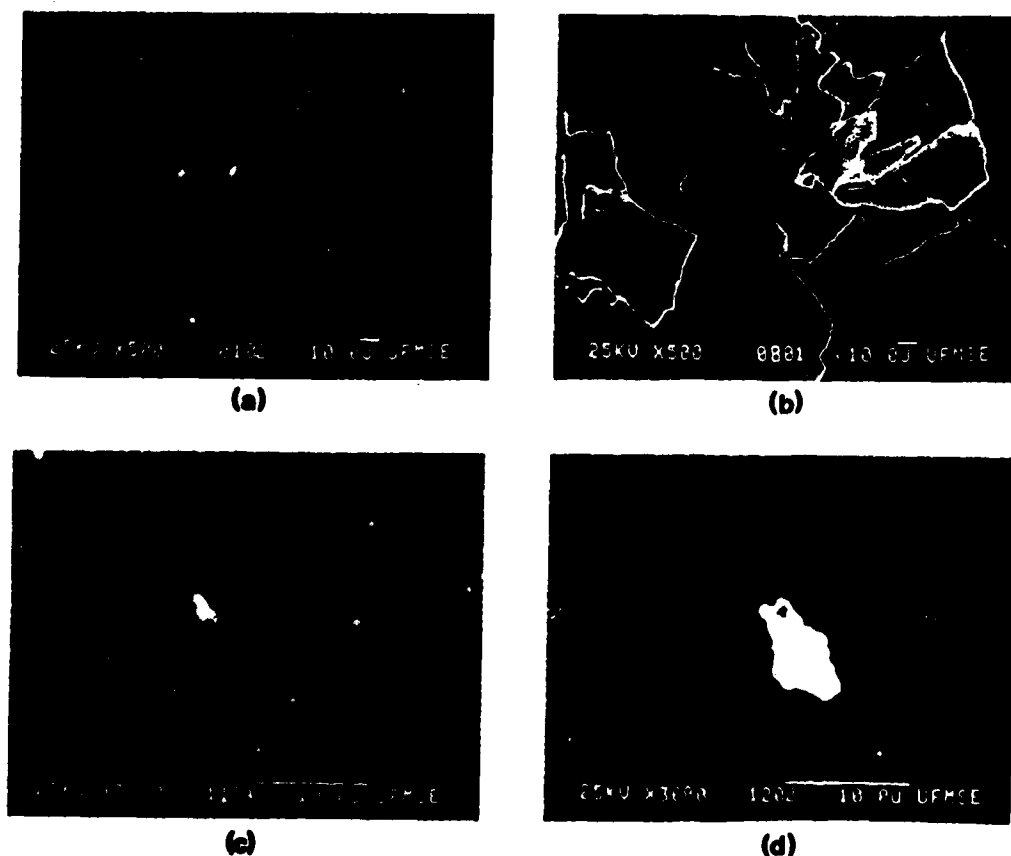
counter electrode and reference electrode, respectively. Monochromatic light (700 nm) generated from a tungsten halogen lamp and monochromator (Oriel #6140 and #7240) was used throughout the experiment.

III. RESULTS

The compositional changes caused by oxygen backfill are shown by Fig. 1 and Table I. From RBS data the average O/

(a)

(b)

(c)

(d)

FIG. 2. Scanning electron micrographs of WO₃ films deposited with $P = 5 \times 10^{-5}$ or 1×10^{-3} Torr oxygen. (a) As-deposited, $P_{0_2} = 5 \times 10^{-5}$ Torr. (b) Same as (a) but after two days in 3.6N H₂SO₄. (c) As-deposited, $P_{0_2} = 1 \times 10^{-3}$ Torr. (d) Same as (c) but after 8 days in 3.6N H₂SO₄.
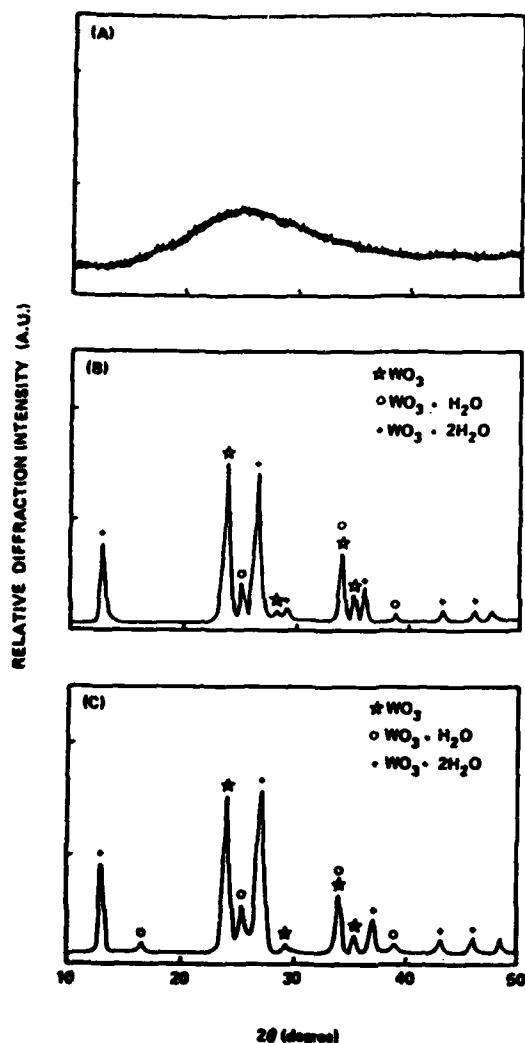
Fig. 3. X-ray diffraction spectra: (A) As-deposited showing amorphous pattern, and (B), (C), from WO₃ films after 18 days in H₂SO₄ where the amorphous background intensity was subtracted to emphasize the crystalline peaks. The spectra are from samples which were deposited with: (B) Residual pressure of 1×10^{-5} Torr, (C) oxygen partial pressure of 1×10^{-3} Torr. The symbols (*, O, +) show the origins of specific diffraction peaks. (*: WO₃, O:WO₃ · H₂O, +:WO₃ · 2H₂O).
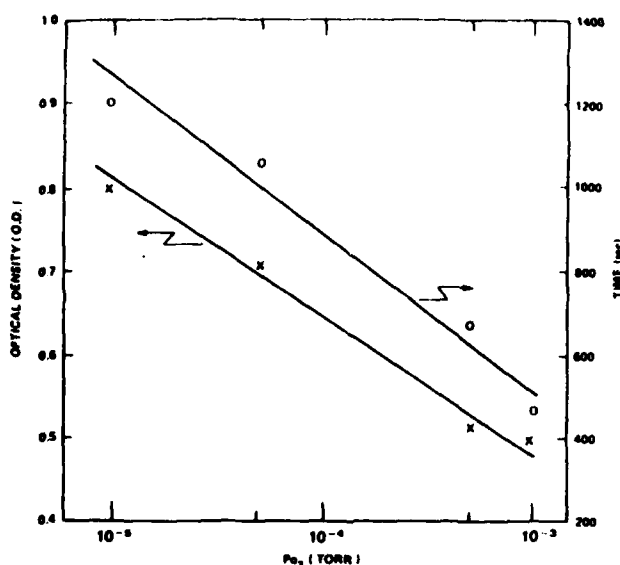

FIG. 4. Oxygen partial pressure vs the maximum optical density or the time for self-erasure to half of the original optical density of WO₃ films ($V_{appl} = -0.6V_{SCE}$, film thickness = 0.3 μm).

substrates. As can be seen in Fig. 2, the films degraded by flaking and delamination. However, films prepared at $P_{O_2} = 1 \times 10^{-3}$ did not show much delamination. For $P_{O_2} > 1 \times 10^{-4}$ Torr, it is apparent at high magnification (3000×) that the corroded surfaces are rougher than the original surfaces are rougher than the original surfaces. X-ray data indi-

faces. X-ray data indicated that all of these initially amorphous films (with or without oxygen backfilling) partially transformed into polycrystalline phases after storage in H₂SO₄ for 18 days. Phases identified by x-ray diffraction were WO₃, WO₃ · H₂O, and WO₃ · 2H₂O (Fig. 3).

The time needed to electrochromically color and bleach films deposited at various pressures are tabulated in Table II. Within experimental error, the coloration time is not significantly changed by oxygen backfilling. However, the bleaching time, the maximum optical absorption (contrast), and the coloration retention time (open circuit memory) all decreased as P_{O_2} increased. The bleaching time decreased from 4.7 s at $P_{res} = 1 \times 10^{-5}$ Torr to 1.6 s at $P_{O_2} = 1 \times 10^{-3}$ Torr. As shown in Fig. 4, films prepared at $P_{res} = 1 \times 10^{-5}$ Torr could be colored to a maximum optical density (OD) of 0.7 with a constant voltage of $-0.6 V_{SCE}$. On the contrary, those prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr could only be colored to a maximum optical density of 0.4. Upon disconnecting the power supply after coloration, the films would self-erase at different rates depending upon the backfill pressure. The time for self-erasure to half of the original OD decreased from 1200 s for films prepared at $P_{res} = 1 \times 10^{-5}$ Torr to 460 s at $P_{O_2} = 1 \times 10^{-3}$ Torr, as shown in Fig. 4.

IV. DISCUSSION

A. Corrosion

Previously, studies have shown that thermally evaporated WO₃ films are:

(a) Amorphous: X-ray diffraction patterns of these films exhibited broad diffuse peaks, but microcrystallites of W–O octahedra with a diameter of 10 Å can be detected by using reflection transmission electron microscopy.[14]

(b) Oxygen deficient: Rutherford backscattering spectrometry has shown that the O/W ratio was 2.76 ± 0.05.[4,11] X-ray photoelectron spectroscopy (XPS) also indicated that

TABLE II. The effect of oxygen backfilling on color/bleach time.

Time (s)/P	1×10^{-5} Torr	5×10^{-5} Torr	5×10^{-4} Torr	1×10^{-3} Torr
Color (t_c)	0.9	1.1	0.9	0.7
Bleach (t_b)	4.7	3.0	2.4	1.6

t_c: Time needed to color the WO₃ films to obtain 10% intensity change.
t_b: Time needed to bleach the WO₃ films to 50% of the original intensity.
$V_{appl} = \pm 0.6 V_{SCE}$.
Thickness: 0.3 μm.

the tungsten atoms exhibit various oxidation states of W^{4+}, W^{5+}, and W^{6+} due to the substoichiometry in these films.[12,15]

(3) Porous: The apparent density is approximately 80% of that of bulk density.[16]

(4) Hydrated: Films contain as much as 0.5 H_2O per WO_3.[7]

Recently, Arnoldussen suggested that WO_3 oxide films formed by thermal evaporation are amorphous molecular solids consisting of trimeric WO_3 molecules bound weakly to each other by water bridging molecules through hydrogen or van der Waals bonds.[13] This model is consistent with the observation of microcrystallites of W–O octahedra, but neglects the fact that the films were substoichiometric and contained W^{4+}, W^{5+}, and W^{6+} oxidation states. Thus, the XPS data suggested that tungsten atoms exist in the molecular solid (deposited films) with configurations at least similar to WO_2, W_2O_5, and WO_3 molecules. These molecules may be linked with each other not only through water bridging molecules as described by Arnoldussen, but also by edge or corner sharing O bonds. The distribution of these molecules may either be a random solution or as aggregated microcrystallites. The data are too sparse to distinguish between these two possibilities. However, both would be consistent with our data and subsequent arguments.

The corrosion of these films in acidic electrolytes can be explained by examining the Pourbaix diagram for tungsten metal.[17] In the storage condition ($E = 0.4$ V_{NHE}, $pH = 0.5$) the WO_3 is the only stable specie. Both WO_2 and W_2O_5 are thermodynamically unstable, however, the conversion processes and products are both unknown. The dissolution of tungstic oxide in acid solution occurs with formation of cationic species such as WO_2^{2+} and WO_2OH^+, whose presence was identified for $pH < 1$ by Nazarrenko et al.[18] DiPaola et al.[19] studied anodic oxide films on tungsten and proposed that for hydration of WO_3, the following reaction takes place:

$$WO_3 + 2H^+ = WO_2^{2+} + H_2O$$

and

$$WO_2^{2+} + (x+1)H_2O = WO_3 \cdot xH_2O + 2H^+,$$
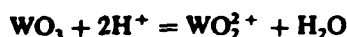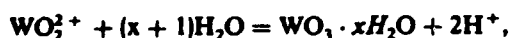
where $x = 1, 2$.

However, the free energy of hydration for forming both the mono- and dihydrate was shown to be positive. The hydration reaction was observed if electrochemically driven or under high temperatures,[19] although the mechanisms for corrosion of WO_2 and W_2O_5 are unknown. It seems reasonable to postulate similar reactions. For example, the dissolution processes may be:

$$WO_2 \rightarrow WO_2^{2+} + 2e^-$$

$$pH < 1,$$

$$W_2O_5 + 2H^+ \rightarrow 2WO_2^{2+} + H_2O + 2e^-,$$

with deposition of WO_3 or hydrated species by the reactions reported above for WO_2^{2+}. The total reaction could then be written as

$$WO_2 + (x+1)H_2O = WO_3 \cdot H_2O + H_2.$$

$$W_2O_5 = (2x+1)H_2O = 2WO_3 \cdot xH_2O + H_2,$$
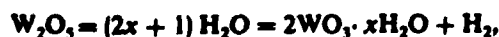
where $x = 0, 1, 2$ and would result in the crystalline phases detected by x-ray diffraction after 18 days storage in acid.

By backfilling during WO_3 evaporation, the oxygen content of WO_3 films was increased. The O/W ratio changed from 2.7 ($P_{res} = 1 \times 10^{-5}$ Torr) to 2.9 $P_{0_2} = 1 \times 10^{-3}$ Torr). These data are comparable to those reported by Deneuville et al. for films evaporated during air backfilling.[4] Since oxygen backfilling increases the O/W ratio to ~3, the films were expected to contain more WO_3 than WO_2 and W_2O_5. Gerard et al. from XPS studies have shown that as O/W increases toward three, the concentration of W^{6+} increases relative to W^{4+} and W^{5+}.[15] Since there are less dissolution-prone species available, the dissolution rate of these oxygen-enriched films in acid electrolytes should decrease. As shown by Fig. 1, the dissolution was negligible when the O/W ratio reached 2.9. However, the dissolution and precipitation of these small amounts of WO_2 and W_2O_5 could rearrange the surface portion of the film to give crystalline peaks of $WO_3 \cdot xH_2O$($x = 0, 1, 2$). The bulk of the films still remains intact. As indicated by Fig. 2, only at higher magnification can the effect be observed—the slightly roughened surface.

The interfacial attack on some films may be induced by: (1) the internal stresses caused by the precipitation of these crystalline phases on the original sample; (2) surface contamination and defects which weaken the adhesion strength of the films to substrate; (3) gas evolution during the transformation; e.g., $2H^+ + 2e^- \rightarrow H_2$. It was observed that less delamination and less dissolution both occurred from films deposited with high oxygen pressure. This would be consistent with precipitation-induced stresses being important. However, small bubbles were also observed on the specimen during corrosion, indicating hydrogen was being evolved. Finally, interfacial attack was minimized for films deposited on the graphite planchetes. The rough surfaces on these substrates may provide a mechanical interlocking through pores and valleys. Thus, surface contamination may also be important. Further data (e.g., residual stress measurement) would be necessary to make a valid choice.

B. Electrochromism

As reported by Haranahalli and Holloway,[6] coloration of deposited films was controlled at short times by the WO_3 resistance and by the mixed barriers (Schottky barrier and Helmholtz double layer) at the interface of electrolyte and WO_3 films. At long times ($t > 1$ s), coloration was controlled by the Helmholtz double layer, which is independent of the film properties. As expected, data in Table II indicate that the oxygen-backfilling does not change the coloration times, which were approximately 1 s.

The bleaching was reported to be limited by proton diffusion in a space-charged region. There are several factors which affect the diffusion of protons in WO_3 films: (1) Amorphism: Crystallization of films is known to decrease the proton diffusion constant by an order of magnitude.[2,5] (2) Water content: Higher water content in the films resulted in faster proton diffusion.[20] (3) Porosity: Higher porosity in the anodic WO_3 films has been shown to increase the bleaching speed.[20] The microstructure of the oxygen-enriched WO₃

films remained amorphous but the porosity increased as indicated by th rougher surface structure for these samples. Matsushiro *et al.*[16] reported the porosity of WO_3 films increased by a factor of 2 when the pressure was increased from 2×10^{-5} to 8×10^{-4} Torr by nitrogen backfilling. The water content in the present films was higher for oxygen backfilling when compared to those with no backfilling as indicated by SIMS data. This should result in higher proton mobility. Therefore, the proton mobility and increased porosity both should result in bleaching speed which are faster for oxygen-enriched films. The data clearly indicate this is the case (Table II).

Hitchman[21] has reported that self-erasure can be caused by the oxidation of HWO_3 back to WO_3 according to the reaction $2HWO_3 + 1/2O_2 = 2WO_3 + H_2O$. The kinetics are controlled by proton diffusion in WO_3 from the bulk to the surface where the reaction takes place. Since the proton mobility was concluded to increase with oxygen backfilling, the self-erasure rate was also expected to increase. This obviously occurred (Fig. 4) along with faster bleaching rates.

The decrement of maximum optical density by oxygen enrichment was also reported by Kaneko *et al.*[22] for their rf reactively sputtered WO_3 films. Arnoldussen[13] had found that oxygen ion implantation of evaporated films results in films which can no longer be colored. This is probably the extreme case. He attributes this phenomenon to the creation of the electron traps of oxygen implantation. Yoshimura *et al.*[23] recently reported that films prepared by evaporation of WO_3 in 1×10^{-4} Torr O_2 also exhibited lower maximum optical density and optical efficiency. They explained these observations by configuration coordinate model[3] and suggested that the oscillator strength of the optical centers decreased as a result of the increase in oxygen. From all these discussions, it is apparent that the change in maximum optical density as a result of oxygen backfilling is related to the oxygen enrichment of these films.

Initially, it was thought that the alkali elements (Na, K) could cause sir ilar changes. However, their concentration $(< 1 \times 10^{19} \text{ cm}^{-3})$ was too low to cause a significant population of electron traps. The change in the population of optical center was calculated to be $6 \times 10^{20} \text{ cm}^{-3}$ which is about two orders of magnitude higher than achievable by alkali elements if each atom resulted in one electron trap. The source of these alkali contaminations is thought to have been desorbed from the fixtures (bell jar, supporting racks, etc.) during deposition. With higher partial pressure of oxygen, a higher evaporation temperature was needed to maintain the same deposition rate as that at lower pressure. Therefore, the alkali desorption from the fixture and walls may occur more readily for deposition at higher pressure.

V. CONCLUSION

Rutherford backscattering spectrometry data indicated that the average O/W ratio for evaporated thin films increased as the oxygen partial pressure was increased. These oxygen-enriched WO_3 films showed negligible dissolution

and delamination in H_2SO_4 when the O/W ratio reached 2.9 (at $P_{0_2} = 1 \times 10^{-3}$ Torr). The Pourbaix diagram for W shows that only WO_3 is thermodynamically stable for this storage condition ($E = 0.4 \text{ V}_{NHE}, pH = 0.5$). Films prepared without oxygen backfilling were substoichiometric (O/W = 2.7) and were found to degrade (dissolve and delaminate) easily in H_2SO_4. This indicates that the tungsten atoms may exist not only as WO_3 but also as thermodynamically unstable WO_2 and W_2O_5, as indicated by x-ray photoelectron spectroscopy data. It was postulated that conversion of WO_2 and W_2O_5 took place as a dissolution and reprecipitation process similar to those for anodic WO_3 films. As a result of the higher stoichiometry of the WO_3 films evaporated in oxygen atmospheres, the concentration of WO_2 and W_2O_5 is lowered and higher stability in acid was observed.

Oxygen backfilling did not change the EC coloration speed since the controlling mechanisms were not affected. Bleaching speeds and self-erasure rates were faster for oxygen-enriched films. These phenomena may result from increased proton mobility due to increased porosity and water content for films prepared at high partial pressure. The lower maximum optical density for oxygen-enriched films was attributed to the creation of deep electron traps or decreased oscillator strength of optical centers.

ACKNOWLEDGMENTS

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